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【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM

SECONDARY BATTERY AND PROCESS FOR PRODUCING IT

5 【SCOPE OF THE CLAIM(S)】

【Claim 1】

A positive electrode active material for a lithium
secondary battery, which comprises a lithium-cobalt
composite oxide represented by the formula $\text{Li}_p\text{Co}_x\text{M}_y\text{O}_z\text{F}_a$
10 (wherein M is a transition metal element other than Co or
an alkaline earth metal element, $0.9 \leq p \leq 1.1$, $0.980 \leq x \leq 1.000$,
 $0 \leq y \leq 0.02$, $1.9 \leq z \leq 2.1$, $x+y=1$ and $0 \leq a \leq 0.02$) and comprising a
mixture containing substantially spherical large
particles of lithium-cobalt composite oxide having an
15 average particle size D50 of from 7 to 20 μm and small
particles of lithium-cobalt composite oxide having an
average particle size D50 of from 10 to 30% of D50 of the
large particles, wherein a mass ratio of the large
particles/the small particles is from 1/2 to 9/1.

20 【Claim 2】

The positive electrode active material according to
Claim 1, wherein the volume basis cumulative size D10 of
the large particles is at least 50% of the average
particle size D50, and the volume basis cumulative size
25 D90 is at most 150% of the average particle size D50.

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【Claim 3】

The positive electrode active material according to Claim 1 or 2, wherein the large particles of the lithium-cobalt composite oxide have a press density of from 2.9
5 to 3.2 g/cm³, and the small particles have a press density of from 2.7 to 3.1 g/cm³.

【Claim 4】

The positive electrode active material according to Claim 1, wherein in the formula, M is at least one member
10 selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Mn, Mg, Ca, Sr, Ba and Al.

【Claim 5】

The positive electrode active material according to any one of Claims 1 to 4, wherein the average particle
15 size D50 is from 5 to 15 μ m, the specific surface area is from 0.3 to 0.7 m²/g, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm1^\circ$ is from 0.07 to 0.14 $^\circ$ as measured by X-ray diffraction using CuK α as a radiation source, and the press density is from 3.1
20 to 3.4 g/cm³.

【Claim 6】

A process for producing the positive electrode active material for a lithium secondary battery as defined in any one of Claims 1 to 5, which comprises
25 mixing substantially spherical large particle size cobalt hydroxide or tricobalt tetraoxide having an average particle size D50 of from 7 to 20 μ m and small particle

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size cobalt hydroxide or tricobalt tetraoxide having an average particle size D50 of from 10 to 30% of the average particle size D50 of the large particles, in a proportion of from 9:1 to 1:2 as the cobalt atomic ratio
5 and mixing a mixture to be obtained and lithium carbonate, followed by firing at a temperature of from 700°C to 1050°C in an oxygen-containing atmosphere.

【Claim 7】

The production process according to Claim 6, wherein
10 the average particle size D10 of the large particle size cobalt hydroxide or tricobalt tetraoxide is at least 50% of the average particle size D50, and the average particle size D90 is at most 150% of the average particle size D50.

15 【Claim 8】

The production process according to Claim 6 or 7, wherein the large particle size cobalt hydroxide or tricobalt tetraoxide has a press density of from 1.7 to 3.0 g/cm³, and the small particle size cobalt hydroxide
20 or tricobalt tetraoxide has a press density of from 1.7 to 3.0 g/cm³.

【Claim 9】

The production process according to any one of Claims 6 to 8, wherein each of the large particle size
25 cobalt hydroxide or tricobalt tetraoxide and the small particle size cobalt hydroxide or tricobalt tetraoxide has a specific surface area of from 2 to 20 m²/g.

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【Claim 10】

The production process according to any one of Claims 6 to 9, wherein the large particle size or small particle size cobalt hydroxide has a half value width of
s the diffraction peak on (001) plane at $2\theta=19\pm1^\circ$ of from 0.18 to 0.35° and a half value width of the diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of from 0.15 to 0.35° , in an X-ray diffraction spectrum using CuK α -ray.

【Claim 11】

10 A positive electrode for a lithium secondary battery, which contains the positive electrode active material as defined in any one of Claims 1 to 5.

【Claim 12】

A lithium secondary battery employing the positive
15 electrode active material as defined in Claim 6.

【DETAILED DESCRIPTION OF THE INVENTION】

【Technical Field to which the Invention Belongs】

The present invention relates to a positive electrode active material for a lithium secondary
20 battery, which has a large volume capacity density and high safety and is excellent in the charge and discharge cyclic durability, a positive electrode for a lithium secondary battery employing it, and a lithium secondary battery.

25 【Prior Art】

Recently, as the portability and cordless tendency of instruments have progressed, a demand for a non-

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aqueous electrolyte secondary battery such as a lithium
secondary battery which is small in size and light in
weight and has a high energy density, has been
increasingly high. As a positive electrode active
5 material for the non-aqueous electrolyte secondary
battery, a composite oxide of lithium and a transition
metal such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiMn_2O_4 or
 LiMnO_2 , has been known.

Among them, a lithium secondary battery using a
10 lithium-cobalt composite oxide (LiCoO_2) as a positive
electrode active material and using a lithium alloy or
carbon such as graphite or carbon fiber as a negative
electrode, can obtain a high voltage at a level of 4V,
whereby it has been widely used as a battery having a
15 high energy density.

However, in a case of the non-aqueous type secondary
battery using LiCoO_2 as a positive electrode active
material, further improvement of the capacity density per
unit volume of a positive electrode layer and the safety,
20 has been desired. On the other hand, there has been a
problem of deterioration of the cyclic properties such as
gradual reduction of the battery discharge capacity due
to repetitive charge and discharge cycle, a problem of
the weight capacity density or substantial reduction of
25 the discharge capacity at a low temperature.

In order to solve a part of these problems, it has
been proposed in JP-A-6-243897 that the average particle

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size of LiCoO_2 as a positive electrode active material, be from 3 to 9 μm , the volume occupied by a group of particles having a particle size of from 3 to 15 μm , be at least 75% of the total volume, and the intensity ratio
5 of the diffraction peaks at $2\theta =$ about 19° and 45° as measured by means of X-ray diffraction using $\text{CuK}\alpha$ as a radiation source, be of a specific value, so that it becomes an active material excellent in the coating properties, the self-discharge properties and the cyclic
10 properties. Further, in the document, it has been proposed that the positive electrode active material is preferably one which does not substantially have such a particle size distribution that the particle size of LiCoO_2 is 1 μm or smaller or 25 μm or larger. With such
15 a positive electrode active material, the coating properties and the cyclic properties have been improved, but, the safety, the volume capacity density and the weight capacity density, have not yet been fully satisfactory.

20 Further, in order to improve the weight capacity density and the charge and discharge cyclic properties of the positive electrode, JP-A-2000-82466 proposes a positive electrode active material wherein the average particle size of lithium-cobalt composite oxide particles
25 is from 0.1 to 50 μm , and at least two peaks are present in the particle size distribution. Further, it has been proposed to mix two types of positive electrode active

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materials having different average particle sizes to prepare a positive electrode active material wherein at least two peaks are present in the particle size distribution. In such a proposal, there may be a case
5 where the weight capacity density and the charge and discharge cyclic properties of the positive electrode can be improved, but on the other hand, there is a complication that the positive electrode material powders having two types of particle size distributions have to
10 be produced, and one satisfying all of the volume capacity density, the safety, the coating uniformity, the weight capacity density and the cyclic properties of the positive electrode, has not yet been obtained.

Further, in order to solve the problem related to
15 the battery characteristics, JP-A-3-201368 proposes to replace 5 to 35% of Co atoms with W, Mn, Ta, Ti or Nb to improve the cyclic properties. Further, JP-A-10-312805 proposes to use hexagonal LiCoO_2 as a positive electrode active material to improve the cyclic properties, wherein
20 the c axis length of the lattice constant is at most 14.051 Å, and the crystal lattice size of (110) direction of the crystal lattice is from 45 to 100 nm.

Further, JP-A-10-72219 proposes that a lithium-cobalt composite oxide of the formula $\text{Li}_x\text{Ni}_{1-y}\text{N}_y\text{O}_2$ (wherein
25 $0 < x < 1.1$, $0 \leq y \leq 1$), of which the primary particles are plate-like or columnar, the ratio of (volume basis cumulative 95% size - volume basis cumulative 5%

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size)/(volume basis cumulative 5% size) is at most 3, and further, the average particle size is from 1 to 50 μm , has a high initial discharge capacity per weight and further is excellent in the charge and discharge cyclic
5 durability.

However, in the prior art, there has been no lithium secondary battery using a lithium-cobalt composite oxide as a positive electrode active material, which sufficiently satisfies all of the volume capacity
10 density, the safety, the coating uniformity, the cyclic properties and further the low temperature properties.

[Problems that the Invention is to Solve]

It is an object of the present invention to provide a positive electrode active material for a lithium
15 secondary battery, which has a large volume capacity density and high safety and is excellent in the charge and discharge cyclic durability, a positive electrode for a lithium secondary battery employing it, and a lithium secondary battery.

20 **[Means of Solving the Problems]**

The present inventors have continued extensive studies to the above object can be achieved by the positive electrode active material having the following constructions.

25 (1) A positive electrode active material for a lithium secondary battery, which comprises a lithium-cobalt composite oxide represented by the formula

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$\text{Li}_p\text{Co}_x\text{M}_y\text{O}_z\text{F}_a$ (wherein M is a transition metal element other than Co or an alkaline earth metal element, $0.9 \leq p \leq 1.1$, $0.980 \leq x \leq 1.000$, $0 \leq y \leq 0.02$, $1.9 \leq z \leq 2.1$, $x+y=1$ and $0 \leq a \leq 0.02$) and comprising a mixture containing

5 substantially spherical large particles of lithium-cobalt composite oxide having an average particle size D50 of from 7 to 20 μm and small particles of lithium-cobalt composite oxide having an average particle size D50 of from 10 to 30% of D50 of the large particles, wherein a

10 mass ratio of the large particles/the small particles is from 1/2 to 9/1.

(2) The positive electrode active material according to the above (1), wherein the volume basis cumulative size D10 of the large particles is at least 50% of the

15 average particle size D50, and the volume basis cumulative size D90 is at most 150% of the average particle size D50.

(3) The positive electrode active material according to any one of the above (1) or (2), wherein the large

20 particles of the lithium-cobalt composite oxide have a press density of from 2.9 to 3.2 g/cm^3 , and the small particles have a press density of from 2.7 to 3.1 g/cm^3 .

(4) The positive electrode active material according to the above (1) to (3), wherein in the formula, M is at

25 least one member selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Mn, Mg, Ca, Sr, Ba and Al.

(5) The positive electrode active material according

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to the above (1) to (4), wherein the average particle size D50 is from 5 to 15 μm , the specific surface area is from 0.3 to 0.7 m^2/g , the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ is from
5 0.07 to 0.14° as measured by X-ray diffraction using $\text{CuK}\alpha$ as a radiation source, and the press density is from 3.1 to 3.4 g/cm^3 .

(6) A process for producing the positive electrode active material for a lithium secondary battery as
10 defined in any one of the above (1) to (5), which comprises mixing substantially spherical large particle size cobalt hydroxide or tricobalt tetraoxide having an average particle size D50 of from 7 to 20 μm and small particle size cobalt hydroxide or tricobalt tetraoxide
15 having an average particle size D50 of from 10 to 30% of the average particle size D50 of the large particles, in a proportion of from 9:1 to 1:2 as the cobalt atomic ratio and mixing a mixture to be obtained and lithium carbonate, followed by firing at a temperature of from
20 700°C to 1050°C in an oxygen-containing atmosphere.

(7) The production process according to the above (6), wherein the average particle size D10 of the large particle size cobalt hydroxide or tricobalt tetraoxide is at least 50% of the average particle size D50, and the
25 average particle size D90 is at most 150% of the average particle size D50.

(8) The production process according to the above

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(6) or (7), wherein the large particle size cobalt hydroxide or tricobalt tetraoxide has a press density of from 1.7 to 3.0 g/cm³, and the small particle size cobalt hydroxide or tricobalt tetraoxide has a press density of
s from 1.7 to 3.0 g/cm³.

(9) The production process according to the above (6) to (8), wherein each of the large particle size cobalt hydroxide or tricobalt tetraoxide and the small particle size cobalt hydroxide or tricobalt tetraoxide
10 has a specific surface area of from 2 to 20 m²/g.

(10) The production process according to any one of the above (6) to (9), wherein the large particle size or small particle size cobalt hydroxide has a half value width of the diffraction peak on (001) plane at $2\theta=19\pm1^\circ$
15 of from 0.18 to 0.35° and a half value width of the diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of from 0.15 to 0.35°, in an X-ray diffraction spectrum using CuK α -ray.

(11) A positive electrode for a lithium secondary
20 battery, which contains the positive electrode active material as defined in any one of the above (1) to (5).

(12) A lithium secondary battery employing the positive electrode active material as defined in the above (6).

25 The reason why an excellent positive electrode active material for a lithium secondary battery as mentioned above can be obtained by the present invention

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is not clear. However, it is considered as follows.
Namely, the positive electrode active material for a
lithium secondary battery of the present invention
comprises a mixture containing large particles and small
5 particles of lithium-cobalt composite oxide having
specific physical properties in a specific ratio.
Therefore, the small particles are filled in the space
among the large particles, and positive electrode active
material to be obtained thereby has a compacted dense
10 structure. This corresponds to that in the present
invention, the shape of the large particles of the
lithium-cobalt composite oxide is spherical, and the
narrower, the surface smoothness or the particle
distribution is, the larger, the volume capacity or the
15 press density of positive electrode active material to be
obtained becomes.

[Mode of Carrying out the Invention]

The lithium-cobalt composite oxide for a positive
electrode of a lithium secondary battery produced in the
20 present invention is represented by the formula
 $\text{Li}_p\text{Co}_x\text{M}_y\text{O}_z\text{F}_a$. In the formula, M, p, x, y, z and a are as
defined above. Particularly, p, x, y, z and a are
preferably as follows. $0.97 \leq p \leq 1.03$, $0.990 \leq x \leq 1.0$,
 $0.0005 \leq y \leq 0.01$, $1.95 \leq z \leq 2.05$, $x+y=1$ and $0.0001 \leq a \leq 0.01$.
25 Here, when a is larger than 0, it is a composite oxide
having some of its oxygen atoms substituted by fluorine
atoms. In such a case, the safety of the obtained

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positive electrode active material will be improved.

Further, M is a transition metal element other than Co, or an alkaline earth metal. The transition metal element represents a transition metal of Group 4, Group 5, Group 6, Group 7, Group 8, Group 9, Group 10 or Group 11 of the Periodic Table. Among them, M is preferably at least one element selected from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Mg, Ca, Sr, Ba and Al. Among them, Ti, Zr, Hf, Mg or Al is preferred from the viewpoint of the volume development properties, the safety, the cyclic durability, etc.

In the present invention, in a case where the above element M and/or F is contained, each of the element M and F is preferably present on the surface of the lithium cobalt oxide particles. If it is present in the interior of the particles, not only the effect of improving the battery characteristics tends to be small, but also the battery characteristics may decrease in some cases. By the presence of these elements on the surface, the important battery characteristics such as the safety or the charge and discharge cyclic properties can be improved by an addition of a small amount without bringing about the reduction of the battery performance. The presence of these elements on the surface can be judged by carrying out a spectroscopic analysis such as a XPS analysis with respect to the positive electrode particles.

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The positive electrode for a lithium secondary battery of the present invention is a lithium-cobalt composite oxide comprising a mixture of large particles of lithium-cobalt composite oxide having the specific average particle size and small particles of lithium-cobalt composite oxide having the specific average particle size in a specific ratio. Here, the average particle sizes D50 is volume basis particle size with respect to the particle size of secondary particles formed by agglomeration and sintering of primary particles, and respectively means the volume basis cumulative 50% size (D50) as particle sizes at points 50% in a cumulative curve prepared by obtaining the particle size distribution on the basis of the volume and bringing the total volume to 100%. The particle size distribution can be obtained by a frequency distribution and cumulative volume distribution curve measured by a laser scattering particle size distribution measuring apparatus. For measurement of the particle size, the particles are sufficiently dispersed in an aqueous medium by e.g. ultrasonic treatment and the particle size distribution is measured (for example, Microtrac HRAX-100 manufactured by Leeds & Northrup is used).

The mixture ratio of the large particles and the small particles is required to be from 1/2 to 9/1 on the basis of mass. If the mixture ratio of the former/the latter is lower than 1/2, the press density of the

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mixture tends to decrease, and on the other hand, if it is higher than 9/1, the press density of the mixture tends to decrease. The mixture ratio of the former/the latter is preferably from 6/4 to 85/15, particularly
5 preferably from 7/3 to 8/2.

The large particles are required to have an average particle size D50 of from 7 to 20 μm and a substantially spherical shape. If the average particle size D50 is smaller than 7 μm , the press density of the mixed powder
10 tends to be low, and on the other hand, if the average particle size D50 is larger than 20 μm , the discharge properties at a large current tend to decrease. Particularly, it tends to be difficult to achieve a volume capacity density. Especially, the average
15 particle size D50 of the large particles is preferably from 9 to 15 μm , particularly preferably from 10 to 14 μm . Further, in the present invention, the large particles being substantially spherical mean that the major axis/minor axis of the particles, i.e. the aspect
20 ratio is preferably from 2/1 to 1/1, particularly preferably from 1.5/1 to 1/1. The large particles preferably have a shape as close to spheres as possible.

Further, the large particles are required to have a narrow particle size distribution so as to achieve a
25 large volume capacity density. With respect to the average particle size distribution, in a case where the average particle sizes respectively means the volume

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basis cumulative 10% size (D10) and 90% size (D90) as particle sizes at points 10% and 90% in a cumulative curve prepared by obtaining the particle size distribution on the basis of the volume and bringing the total volume to 100%, D10 is preferably at least 50% of the above D50, particularly preferably at least 65%, and D90 is preferably at most 150% of the above D50, particularly preferably at most 135%. Further, the surface of the large particles is preferably as smooth as possible.

On the other hand, the small particles of the lithium-cobalt composite oxide preferably have an average particle size D50 of from 10 to 30% of D50 of the above large particles. If the average particle size D50 of the small particles is smaller than 10% of D50 of the large particles, the press density of the mixture tends to decrease, and the safety tends to decrease. On the other hand, if it is larger than 30% of D50 of the large particles, the effect of improving the press density of the mixture tends to decrease. Accordingly, the average particle size D50 of the small particles is preferably from 15 to 25% of D50 of the large particles. The small particles of lithium-cobalt composite oxide do not necessarily have a specific shape, but they may have various shapes such as spheres, columns and blocks.

Further, the large particles and the small particles of lithium-cobalt composite oxide preferably have press

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densities of from 2.8 to 3.2 g/cm³ and from 2.7 to 3.2 g/cm³, respectively. In the present invention, the press density means an apparent press density when the particle powder is press-compressed under a pressure of 0.3 t/cm²,
5 unless otherwise specified. If the press density of the large particles or the small particles is lower than the above range, the press density of the mixture tends to decrease, and on the other hand, if it is higher than the above range, the discharge properties at a large current
10 tend to decrease. It is preferred that the large particles and the small particles have press densities of from 2.9 to 3.1 g/cm³ and from 2.8 to 3.0 g/cm³, respectively. Further, the lithium composite oxide has a remaining alkali amount contained therein of preferably
15 at most 0.02 mass%, particularly preferably at most 0.01 mass%.

The large particles and the small particles forming the above lithium-cobalt composite oxide may be produced by various processes, and the production methods are
20 not particularly limited, however, they are produced preferably as follows. For example, a mixture containing a cobalt source, a lithium source, and an element M source and a fluorine source used as the case requires, is fired in an oxygen-containing atmosphere at a
25 temperature of from 700 to 1050°C. The cobalt source may, for example, be tricobalt tetraoxide, cobalt oxyhydroxide or cobalt hydroxide, and the lithium source

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may, for example, be lithium carbonate or lithium hydroxide. At that time, the physical property values such as the size, the shape and the particle size distribution of the lithium-cobalt composite oxide particles to be produced can be controlled particularly by controlling the particle size, the particle shape, the particle size distribution and the specific surface area of the above cobalt source.

A mixture comprising the obtained mixture and a lithium source, and a material of the element M and a fluorine source is fired in an oxygen-containing atmosphere at from 700 to 1,050°C, particularly preferably from 900 to 1,000°C, for preferably from 5 to 20 hours. The fired product to be obtained is cooled, followed by pulverization and classification, and thus the lithium-cobalt composite oxide particles can be produced. In a case of employing tricobalt tetraoxide as the cobalt source, powder having an average particle size of from 1 to 20 μm and a specific surface area of from 0.5 to 5 m^2/g is preferably used. In a case of employing cobalt oxyhydroxide as the cobalt source, powder having the average particle size D50 of from 1 to 20 μm and a specific surface area of from 2 to 200 m^2/g is preferably used. The average particle size D50 of cobalt oxyhydroxide is particularly preferably from 4 to 15 μm .

In a case of employing lithium hydroxide as the lithium source, powder having the average particle size

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D50 of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g is preferably used. For the lithium-cobalt composite oxide of the present invention, plural cobalt sources are used. For example, a combination of
5 cobalt hydroxide and tricobalt tetraoxide and a combination of tricobalt tetraoxide having a large particle size and tricobalt tetraoxide having a small particle size may be mentioned, and the lithium-cobalt composite oxide of the present invention can be
10 preferably produced by mixing firing starting material containing such cobalt sources and lithium carbonate.

As a preferred process for producing the lithium-cobalt composite oxide of the present invention, the following process may be mentioned. Namely,
15 substantially spherical large particles of cobalt hydroxide or tricobalt tetraoxide having the average particle size D50 of from 7 to 20 μm and small particles of cobalt hydroxide or tricobalt tetraoxide having an average particle size D50 of from 10 to 30% of the
20 average particle size D50 of the large particles are mixed in a proportion of from 9:1 to 1:2 as the cobalt atomic ratio. A mixture comprising the obtained mixture and a lithium source is fired in an oxygen-containing atmosphere at from 700 to 1,050°C, particularly
25 preferably from 900 to 1,000°C.

In such a case, the large particles of cobalt hydroxide or tricobalt tetraoxide are required to have an

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average particle size D10 of at least 50% of the average particle size D50 and an average particle size D90 of at most 150% of the average particle size D50, whereby an effect of improving the press density of the positive
5 electrode will be obtained. Further, it is preferred that the large particles of cobalt hydroxide or tricobalt tetraoxide have a press density of from 1.7 to 3.0 g/cm³ and that the small particles of cobalt hydroxide or tricobalt tetraoxide have a press density of from 1.7 to
10 3.0 g/cm³. Further, it is preferred that each of the large particles and the small particles of cobalt hydroxide or tricobalt tetraoxide have a specific surface area of from 2 to 20 m²/g.

Further, the large particles of cobalt hydroxide or
15 the small particles of cobalt hydroxide have, in an X-ray diffraction spectrum using CuK α -ray, a half value width of the diffraction peak on (001) plane at $2\theta=19.1\pm1^\circ$ of preferably from 0.18 to 0.35°, particularly preferably from 0.22 to 0.30°, and a half value width of the
20 diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of preferably from 0.15 to 0.35°, particularly preferably from 0.18 to 0.30°. When the half value widths are within the above ranges, effects of improving the safety and the press density of the positive electrode will be obtained.

25 To produce a positive electrode for a lithium secondary battery from the lithium-cobalt composite oxide of the present invention, a carbon type conductive

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material such as acetylene black, graphite or Ketjenblack and a binding material are mixed with a powder of the composite oxide. As the binding material, preferably polyvinylidene fluoride, polytetrafluoroethylene,
5 polyamide, carboxymethyl cellulose or acrylic resin may, for example, be used.

The powder of the lithium-cobalt composite oxide, the conductive material and the binding material are formed into a slurry or a kneaded product by using a
10 solvent or a dispersion medium, which is supported on a positive electrode current collector such as aluminum foil or stainless steel foil by e.g. coating to form a positive electrode plate for a lithium secondary battery.

In a lithium secondary battery using the lithium-
15 cobalt composite oxide of the present invention as the positive electrode active material, as the separator, a porous polyethylene or a porous propylene film may be used. Further, as a solvent of the electrolyte solution of the battery, various solvents may be used. However, a
20 carbonate ester is preferred. As the carbonate ester, each of a cyclic type and a chain type can be used. As the cyclic carbonate ester, propylene carbonate or ethylene carbonate (EC) may, for example, be mentioned. As the chain carbonate ester, dimethyl carbonate, diethyl
25 carbonate (DEC), ethyl methyl carbonate (EMC), methyl propyl carbonate or methyl isopropyl carbonate may, for example, be mentioned.

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In the present invention, the carbonate ester may be used alone or by mixing at least two types. Further, it may be used by mixing with another solvent. Further, according to the material of the negative electrode
5 active material, if the chain carbonate ester is used together with the cyclic carbonate ester, there is a case where the discharge properties, the cyclic durability or the charge and discharge efficiency can be improved.

Further, in the lithium secondary battery using the
10 lithium-cobalt composite oxide of the present invention as the positive electrode active material, a gel polymer electrolyte containing a vinylidene fluoride-hexafluoropropylene copolymer (for example, KYNAR manufactured by ELF Atochem) or a vinylidene fluoride-
15 perfluoropropyl vinyl ether copolymer may be employed. As the solute to be added to the electrolyte solvent or the polymer electrolyte, at least one member of lithium salts is preferably used, wherein e.g. ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ is anion.
20 It is preferably added at a concentration of from 0.2 to 2.0 mol/L to the electrolyte solvent or the polymer electrolyte comprising the lithium salt. If the concentration departs from this range, ionic conductivity will decrease, and the electrical conductivity of the
25 electrolyte will decrease. More preferably, it is from 0.5 to 1.5 mol/L.

In the lithium battery using the lithium-cobalt

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composite oxide of the present invention as the positive electrode active material, as the negative electrode active material, a material which can occlude and discharge lithium ions may be used. The material forming
5 the negative electrode active material is not particularly limited, however, lithium metal, a lithium alloy, a carbon material, an oxide comprising, as a main body, a metal of Group 14 or Group 15 of the Periodic Table, a carbon compound, a silicon carbide compound, a
10 silicone oxide compound, titanium sulfide or a boron carbide compound may, for example, be mentioned. As the carbon material, an organic material which is subjected to thermal decomposition under various thermal decomposition conditions, artificial graphite, natural
15 graphite, soil graphite, exfoliated graphite or squamation graphite etc. can be used. Further, as the oxide, a compound comprising tin oxide as a main body can be used. As the negative electrode current collector, a copper foil, a nickel foil etc. can be used. The
20 negative electrode is produced preferably by kneading the active material with an organic solvent to form a slurry, which is coated on the metal foil current collector, dried and pressed.

The shape of the lithium battery using the lithium-
25 cobalt composite oxide of the present invention as the positive electrode active material is not particularly limited. Sheet, film, folding, winding type cylinder

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with bottom or button shape etc. is selected according to use.

[Examples]

Now, the present invention will be explained in further detail with reference to Examples. However, the present invention is by no means restricted to such specific Examples. Examples 1 to 4, 11 to 14 and 15 to 17 are Examples of the present invention, and Examples 5 to 8, 10 and 15 are Comparative Examples.

10 **EXAMPLE 1**

A spherical cobalt hydroxide powder formed by agglomeration of primary particles having, in powder X-ray diffraction using $\text{CuK}\alpha$ -ray, a half value width of the diffraction peak on (001) plane at $2\theta=19\pm1^\circ$ of 0.28° and 15 a half value width of the diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of 0.21° , average particle sizes D50 of $16.7\ \mu\text{m}$, D10 of $13.4\ \mu\text{m}$ and D90 of $21.1\ \mu\text{m}$, and a specific surface area of $3.6\ \text{m}^2/\text{g}$, and a lithium carbonate powder having a specific surface area of $1.2\ \text{m}^2/\text{g}$, were mixed. 20 They were blended in such a mixture ratio that the composition would be LiCoO_2 after firing. After dry mixing of these two types of powders, the mixture was fired in the air atmosphere at 950°C for 12 hours.

The fired product was crushed, and the particle size 25 distribution of the obtained large particle size LiCoO_2 powder formed by agglomeration of primary particles was measured by using a laser scattering type particle size

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distribution measuring apparatus and as a result, the average particle size D50 was 13.4 μm , D10 was 10.2 μm , and D90 was 17.4 μm , and a large particle size spherical LiCoO_2 powder having a specific surface area of 0.32 m^2/g as obtained by BET method was obtained. The LiCoO_2 powder had D10/D50 of 76% and D90/D50 of 130%, and has a considerably narrow particle size distribution.

With respect to the LiCoO_2 powder, observation by an electron microscope at magnifications of 1,000 and 5,000 was carried out, to measure the average of the proportion of the major axis to the minor axis (aspect ratio) of 500 spherical particles at each magnification. As a result, the average was 1.16, and the powder was found to have a shape close to spheres. The surface was smooth. With respect to the LiCoO_2 powder, an X-ray diffraction spectrum was obtained by using an X-ray diffraction apparatus (RINT 2100 manufactured by Rigaku Corporation). In powder X-ray diffraction using $\text{CuK}\alpha$ -ray, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ was 0.089° . The above large particle size spherical LiCoO_2 powder will be referred to as "powder A".

On the other hand, a particulate cobalt hydroxide powder having average particle sizes D50 of 0.6 μm , D10 of 0.3 μm and D90 of 1.3 μm and a specific surface area of 17.1 m^2/g , and a lithium carbonate powder having a specific surface area of 1.2 m^2/g , were mixed. They were

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blended in such a mixture ratio that the composition would be LiCoO_2 after firing. After dry mixing of these two types of powders, the mixture was fired in the air atmosphere at 950°C for 12 hours. The fired product was
5 crushed, and the particle size distribution of the obtained small particle size LiCoO_2 powder was measured by using a laser scattering type particle size distribution measuring apparatus and as a result, the average particle size D50 was $2.6\ \mu\text{m}$, D10 was $1.5\ \mu\text{m}$ and
10 D90 was $5.6\ \mu\text{m}$, and an aggregated LiCoO_2 powder having a specific surface area of $0.53\ \text{m}^2/\text{g}$ as obtained by BET method was obtained.

With respect to this aggregated LiCoO_2 powder, observation by an electron microscope at magnifications
15 of 1,000, 5,000 and 10,000 was carried out and as a result, it was found that from about 3 to about 20 particles of from 2 to $4\ \mu\text{m}$ were agglomerated to form a non-spherical aggregate. With respect to the LiCoO_2 powder, an X-ray diffraction spectrum was obtained by
20 using an X-ray diffraction apparatus (RINT 2100 manufactured by Rigaku Corporation). In powder X-ray diffraction using $\text{CuK}\alpha$ -ray, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ was 0.097° . The above small particle size spherical LiCoO_2 powder
25 will be referred to as "powder B". The powder B had a D50 of 19% of D50 of the powder A. 60 Parts by weight of the powder A and 40 parts by weight of the powder B were

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mixed, and the obtained mixed powder was pressed by an oil hydraulic pressing machine under 0.3 t/cm^2 , whereupon the apparent density after pressing was 3.20 g/cm^3 . 10 g of the LiCoO_2 powder was dispersed in 100 g of pure
5 water, and after filtration, the remaining alkali amount was obtained by potentiometric titration with 0.1 N HCl and found to be 0.02 wt%.

The above LiCoO_2 mixed powder, acetylene black and a polyvinylidene fluoride powder were mixed in a mass ratio
10 of 90/5/5, and N-methylpyrrolidone was added thereto to prepare a slurry, which was coated on one side of an aluminum foil having a thickness of $20 \text{ }\mu\text{m}$ by using a Doctor Blade. After drying, roll press rolling was carried out once to prepare a positive electrode body
15 sheet for a lithium battery. The density of the electrode layer was measured from the thickness of the positive electrode body after rolling and the weight per unit area of the electrode layer and found to be 3.37 g/cm^3 .

20 Then, using one punched out from the positive electrode body sheet as a positive electrode, using a metal lithium foil with a thickness of $500 \text{ }\mu\text{m}$ as a negative electrode, using $20 \text{ }\mu\text{m}$ of a nickel foil as a negative electrode current collector, using a porous
25 polypropylene with a thickness of $25 \text{ }\mu\text{m}$ as a separator, and using as an electrolyte solution a $1\text{M LiPF}_6/\text{EC}+\text{DEC}$ (1:1) solution (it means a mixed solution of EC and DEC

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in a mass ratio (1:1) comprising LiPF_6 as a solute, the same applies hereinafter), two pieces of simplifying sealed cell type lithium batteries made of stainless steel were assembled in an argon globe box.

5 One of these batteries employing the EC+DEC (1:1) solution as the electrolyte solution was charged up to 4.3 V at a load current of 75 mA per 1 g of the positive electrode active material at 25°C, and discharged down to 2.5 V at a load current of 75 mA per 1 g of the positive
10 electrode active material, whereby the initial discharge capacity was obtained. Further, the volume capacity density was obtained from the density of the electrode layer and the capacity per weight. With respect to this battery, the charge and discharge cycle test was further
15 carried out 30 times. As a result, the initial volume capacity density of the positive electrode layer at 25°C at a voltage of from 2.5 to 4.3 V was 451 mAh/cm³ electrode layer, the initial weight capacity density was 159 mAh/g- LiCoO_2 , and the capacity retention ratio after
20 30 times of charge and discharge cycle, was 97.3%. Further, with respect to the other battery employing the EC+DEC (1:1) solution as the electrolyte solution, the other battery was charged for 10 hours at 4.3 V, and then broken down in the argon globe box. The positive
25 electrode body sheet was picked up after charge, and after the positive electrode body sheet was washed, it was punched out at a radius of 3 mm, and then sealed in

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an aluminum capsule with EC. And then, it was heated at a rate of 5°C/min by using a scanning differential calorimeter, whereby the heat generation starting temperature was measured. As a result, the heat
5 generation starting temperature of the 4.3 V charged product was 160°C.

EXAMPLE 2

A mixed powder was obtained in the same manner as in Example 1 except that 80 parts by weight of the powder A
10 and 20 parts by weight of the powder B were mixed. The mixed powder after pressing had an apparent density of 3.23 g/cm³. Further, by using this powder, in the same manner as in Example 1, a positive electrode was produced, batteries were assembled, and the properties
15 were measured. The weight capacity density was 160 mAh/g, the capacity retention ratio after 30 times of charge and discharge cycle was 97.5%, and the heat generation starting temperature was 163°C.

EXAMPLE 3

20 A mixed powder was obtained in the same manner as in Example 1 except that 40 parts by weight of the powder A and 60 parts by weight of the powder B were mixed. The mixed powder after pressing had an apparent density of 3.13 g/cm³. Further, by using this powder, in the same
25 manner as in Example 1, a positive electrode was produced, batteries were assembled, and the properties were measured. The weight capacity density was 160

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mAh/g, the capacity retention ratio after 30 times of charge and discharge cycle was 97.2%, and the heat generation starting temperature was 160°C.

EXAMPLE 4

5 In Example 1, a spherical cobalt hydroxide powder from a material having a different particle size distribution was used as the material cobalt hydroxide for large particles, instead of the powder A. In the same manner as in Example 1, the powder was mixed with
10 lithium carbonate and fired, and the fired product was crushed, and the particle size distribution of the obtained large particle size LiCoO_2 powder was measured by using a laser scattering type particle size distribution measuring apparatus and as a result, the
15 average particle size D50 was 13.0 μm , D10 was 7.9 μm and D90 was 18.9 μm , and a large particle size spherical LiCoO_2 powder having a specific surface area of 0.35 m^2/g as obtained by BET method was obtained. This LiCoO_2 powder had D10/D50 of 61% and D90/D50 of 145%, and has a
20 narrow particle size distribution.

 With respect to this LiCoO_2 powder, observation by an electron microscope at magnifications of 1,000 and 5,000 was carried out to measure the average of the proportion of the major axis to the minor axis (aspect ratio) of 500
25 spherical particles at each magnification. As a result, the average was 1.14, and the particles were found to have a shape close to spheres. The above large particle

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size spherical LiCoO_2 powder will be referred to as "powder E". A mixed powder was obtained in the same manner as in Example 1 except that 60 parts by weight of the powder E and 40 parts by weight of the powder B were
5 mixed. The powder B had a D50 of 20% of D50 of the powder E. The mixed powder after pressing had an apparent density of 3.14 g/cm^3 . The weight capacity density of a positive electrode employing this mixed powder was 160 mAh/g , the capacity retention ratio after
10 30 times of charge and discharge cycle was 97.4%, and the heat generation starting temperature was 161°C .

EXAMPLE 5

The apparent density after pressing obtained in the same manner as in Example 1 except that the powder A
15 alone was used in Example 1 was 2.95 g/cm^3 . As a result, the initial weight capacity density at 25°C at from 2.5 to 4.3 V was $160 \text{ mAh/g-LiCoO}_2$, the capacity retention ratio after 30 times of charge and discharge cycle was 97.1%, and the heat generation starting temperature of a
20 4.3 V charged product was 163°C .

EXAMPLE 6

The apparent density after pressing obtained in the same manner as in Example 1 except that the powder B
alone was used in Example 1 was 2.78 g.cm^3 . As a result,
25 the initial weight capacity density at 25°C at from 2.5 to 4.3 V was $159 \text{ mAh/g-LiCoO}_2$, the capacity retention ratio after 30 times of charge and discharge cycle was

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97.0%, and the heat generation starting temperature of a 4.3 V charged product was 158°C.

EXAMPLE 7

A mixed powder was obtained in the same manner as in
5 Example 1 except that 20 parts by weight of the powder A and 80 parts by weight of the powder B were mixed in Example 1. The mixed powder after pressing had an apparent density of 3.03 g/cm³. The weight capacity
10 density of a positive electrode employing this mixed powder was 159 mAh/g, the capacity retention ratio after 30 times of charge and discharge cycle was 97.0%, and the heat generation starting temperature was 159°C.

EXAMPLE 8

A mixed powder was obtained in the same manner as in
15 Example 1 except that 95 parts by weight of the powder A and 5 parts by weight of the powder B were mixed in Example 1. The mixed powder after pressing had an apparent density of 3.05 g/cm³. The weight capacity
20 density of a positive electrode employing this mixed powder was 159 mAh/g, the capacity retention ratio after 30 times of charge and discharge cycle was 97.0%, and the heat generation starting temperature was 158°C.

EXAMPLE 9

The apparent density after pressing obtained in the
25 same manner as in Example 1 except that the powder E alone was used in Example 4 was 3.02 g/cm³. The weight capacity density of a positive electrode employing this

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mixed powder was 159 mAh/g, the capacity retention ratio after 30 times of charge and discharge cycle was 97.0%, and the heat generation starting temperature was 160°C.

EXAMPLE 10

5 Commercially available cobalt hydroxide was used as small particle size cobalt hydroxide. As a result of observation by a scanning electron microscope of the small particle size cobalt hydroxide, it was found that aggregated secondary particles consisting of several to
10 about twenty primary particles were formed. The cobalt hydroxide particles consisting of the secondary particles had a specific surface area of $2.4 \text{ m}^2/\text{g}$, and had an apparent density of 2.21 g/cm^3 after pressed by an oil hydraulic pressing machine under 0.3 t/cm^2 . The small
15 particle size cobalt hydroxide had, in powder X-ray diffraction using $\text{CuK}\alpha$ -ray, a half value width of the diffraction peak on (001) plane at $2\theta=19\pm1^\circ$ of 0.16° and a half value width of the diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of 0.15° . The particle size distribution of
20 the powder of the secondary particles was measured by using a laser scattering type particle size distribution measuring apparatus employing water as a dispersion medium and as a result, the average particle size D50 was $3.5 \text{ }\mu\text{m}$, D10 was $0.3 \text{ }\mu\text{m}$ and D90 was $7.6 \text{ }\mu\text{m}$.

25 On the other hand, a mixed liquid of an aqueous cobalt sulfate solution and ammonium hydroxide, and an aqueous caustic soda solution, were continuously mixed to

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continuously synthesize a cobalt hydroxide slurry by a known method, and by means of aggregation, filtration and drying steps, a large particle size substantially spherical cobalt hydroxide powder was obtained. The
5 obtained cobalt hydroxide had, in powder X-ray diffraction using $\text{CuK}\alpha$ -ray, a half value width of the diffraction peak on (001) plane at $2\theta=19\pm1^\circ$ of 0.28° and a half value width of the diffraction peak on (101) plane at $2\theta=38\pm1^\circ$ of 0.21° . The particle size distribution of
10 the powder of the secondary particles was measured by using a laser scattering type particle size distribution measuring apparatus employing water as a dispersion medium and as a result, the average particle size D50 was $16.7\text{ }\mu\text{m}$, D10 was $13.4\text{ }\mu\text{m}$ and D90 was $21.1\text{ }\mu\text{m}$, and D10 was
15 80% of D50 and D90 was 126% of D50. Further, the specific surface area was $3.6\text{ m}^2/\text{g}$, the press density was 2.11 g/cm^3 , and as a result of observation by a scanning electron microscope, the powder was a cobalt hydroxide powder consisting of substantially spherical large
20 particles formed by strong agglomeration of dozens or more needle primary particles. Further, the aspect ratio was obtained with respect to 500 particles and as a result, the proportion of major axis/minor axis was 1.20/1 on the average.

25 These two types of cobalt hydroxide powders and a lithium carbonate powder having a specific surface area of $1.2\text{ m}^2/\text{g}$ were mixed. The mixture ratio of the large

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particle size cobalt hydroxide to the small particle size cobalt hydroxide was 75:25 (weight ratio). The small particle size cobalt hydroxide had a D50 of 21% of D50 of the large particle size cobalt hydroxide. These two
5 types of the cobalt hydroxide powders and the lithium carbonate powder were blended in such a mixture ratio that the composition would be LiCoO_2 after firing. After dry mixing of these three types of powders, the mixture was fired in the air atmosphere at 950°C for 12 hours.
10 The fired product was crushed, and the particle size distribution of the obtained LiCoO_2 powder formed by agglomeration of the primary particles was measured by using a laser scattering type particle size distribution measuring apparatus employing water as a dispersion
15 medium and as a result, the average particle size D50 was $14.6\text{ }\mu\text{m}$, D10 was $12.1\text{ }\mu\text{m}$ and D90 was $18.0\text{ }\mu\text{m}$, and a LiCoO_2 powder having a specific surface area of $0.37\text{ m}^2/\text{g}$ as obtained by BET method was obtained.

With respect to the LiCoO_2 powder, an X-ray
20 diffraction spectrum was obtained by using an X-ray diffraction apparatus (RINT 2100 manufactured by Rigaku Corporation). In powder X-ray diffraction using $\text{CuK}\alpha$ -ray, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ was 0.101° . The LiCoO_2 powder
25 had a press density of 3.27 g/cm^3 . The alkali content was 0.02 wt%.

The above LiCoO_2 mixed powder, acetylene black and a

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polyvinylidene fluoride powder were mixed in a mass ratio of 90/5/5, and N-methylpyrrolidone was added thereto to prepare a slurry, which was coated on one side of an aluminum foil having a thickness of 20 μm by using a Doctor Blade. After drying, roll press rolling was carried out five times to prepare a positive electrode body sheet for a lithium battery. The density of the electrode layer was measured from the thickness of the positive electrode body after rolling and the weight per unit area of the electrode layer and found to be 3.45 g/cm^3 .

Then, using one punched out from the positive electrode body sheet as a positive electrode, using a metal lithium foil with a thickness of 500 μm as a negative electrode, using 20 μm of a nickel foil as a negative electrode current collector, using a porous polypropylene with a thickness of 25 μm as a separator, and using as an electrolyte solution a 1M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (1:1) solution (it means a mixed solution of EC and DEC in a mass ratio (1:1) comprising LiPF_6 as a solute, the same applies hereinafter), two pieces of simplifying sealed cell type lithium batteries made of stainless steel were assembled in an argon globe box.

One of these batteries employing the EC+DEC (1:1) solution as the electrolyte solution was charged up to 4.3 V at a load current of 75 mA per 1 g of the positive electrode active material at 25°C, and discharged down to

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2.5 V at a load current of 75 mA per 1 g of the positive electrode active material, whereby the initial discharge capacity was obtained. Further, the volume capacity density was obtained from the density of the electrode layer and the capacity per weight. With respect to this battery, the charge and discharge cycle test was further carried out 30 times. As a result, the initial volume capacity density of the positive electrode layer at 25°C at a voltage of from 2.5 to 4.3 V was 465 mAh/cm³ electrode layer, the initial weight capacity density was 160 mAh/g-LiCoO₂, and the capacity retention ratio after 30 times of charge and discharge cycle, was 97.2, and the heat generation starting temperature was 161°C.

EXAMPLE 11

In the same manner as in Example 1 except that the mixture ratio of the large particle size cobalt hydroxide to the small particle size cobalt hydroxide was 50:50 (weight ratio) in Example 10, a LiCoO₂ powder was synthesized. The small particle size cobalt hydroxide had a D50 of 21% of D50 of the large particle size cobalt hydroxide. The cobalt hydroxide powders and the cobalt carbonate were blended in such a mixture ratio that the composition would be LiCoO₂ after firing. LiCoO₂ had average particle sizes D50 of 12.5 μm, D10 of 10.3 μm and D90 of 17.2 μm, and a LiCoO₂ powder having a specific surface area of 0.42 m²/g as obtained by BET method was obtained. With respect to the LiCoO₂ powder, an X-ray

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diffraction spectrum was obtained by using an X-ray diffraction apparatus (RINT 2100 manufactured by Rigaku Corporation). In powder X-ray diffraction using CuK α -ray, the half value width of the diffraction peak on
5 (110) plane at $2\theta=66.5\pm1^\circ$ was 0.102° . The obtained LiCoO₂ powder had a press density of 3.24 g/cm^3 .

As a result, the initial weight capacity density at 25°C at from 2.5 to 4.3 V was $161 \text{ mAh/g-LiCoO}_2$, and the capacity retention ratio after 30 times of charge and
10 discharge cycle was 97.5%. Further, the heat generation starting temperature of a 4.3 V charged product was 162°C .

EXAMPLE 12

In Example 10, large particle size cobalt hydroxide
15 was fired in the air atmosphere at a firing temperature of 900°C for 12 hours to synthesize large particle size substantially spherical tricobalt tetraoxide. The synthesized tricobalt tetraoxide had, in powder X-ray diffraction using CuK α -ray, the half value width of the
20 diffraction peak on (220) plane at $2\theta=31\pm1^\circ$ of 0.15° and a half value width of the diffraction peak on (311) plane at $2\theta=37\pm1^\circ$ of 0.16° . As a result of measurement by using a laser scattering type particle size distribution measuring apparatus employing water as a dispersion
25 medium, the average particle size D50 was $15.5 \mu\text{m}$, D10 was $12.8 \mu\text{m}$ and D90 was $19.1 \mu\text{m}$, the specific surface area was $3.6 \text{ m}^2/\text{g}$, the press density was 2.30 g/cm^3 , and

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the powder was a substantially spherical tricobalt tetraoxide powder formed by strong agglomeration of needle primary particles.

In the same manner as in Example 11 except that the
5 substantially spherical large particle size tricobalt tetraoxide powder and the small particle size cobalt hydroxide of Example 11 were used, a LiCoO_2 powder was synthesized. The mixture ratio of the tricobalt tetraoxide powder to the small particle size cobalt
10 hydroxide of Example 11 was 75:25 as the cobalt atomic ratio. The small particle size cobalt hydroxide had a D50 of 23% of D50 of the large particle size tricobalt tetraoxide. The cobalt hydroxide, the tricobalt tetraoxide and lithium carbonate were blended in such a
15 mixture ratio that the composition would be LiCoO_2 after firing. As a result of measurement by using a laser scattering type particle size distribution measuring apparatus employing water as a dispersion medium, LiCoO_2 had average particle sizes D50 of 14.3 μm , D10 of 11.5 μm
20 and D90 of 18.1 μm , and a LiCoO_2 powder having a specific surface area of 0.40 m^2/g as obtained by BET method was obtained. With respect to the LiCoO_2 powder, an X-ray diffraction spectrum was obtained by using an X-ray diffraction apparatus (RINT 2100 manufactured by Rigaku
25 Corporation). In powder X-ray diffraction using $\text{CuK}\alpha$ -ray, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ was 0.099° . The obtained

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LiCoO₂ powder had a press density of 3.26 g/cm³.

As a result, the initial weight capacity density at 25°C at from 2.5 to 4.3 V was 161 mAh/g-LiCoO₂, the capacity retention ratio after 30 times of charge and
5 discharge cycle was 97%. Further, the heat generation starting temperature of a 4.3 V charged product was 164°C.

EXAMPLE 13

In the same manner as in Example 11 except that a
10 titanium oxide powder and a lithium fluoride powder were further added when the two types of the cobalt hydroxide powders and the lithium carbonate powder were mixed in Example 10, a positive electrode active material was synthesized. As a result of elemental analysis, the
15 positive electrode active material was found to be LiCo_{0.997}Ti_{0.003}O_{1.998}F_{0.002}. The fired product was crushed, and the particle size distribution of the obtained powder of the above composition, formed by agglomeration of primary particles, was measured by using a laser
20 scattering type particle size distribution measuring apparatus employing water as a dispersion medium and as a result, the average particle size D50 was 13.2 μm, D10 was 10.1 μm and D90 was 16.3 μm, and a substantially spherical LiCoO₂ powder having a specific surface area of
25 0.48 m²/g as obtained by BET method was obtained.

With respect to the above powder, an X-ray diffraction spectrum was obtained by using an X-ray

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diffraction apparatus (RINT 2100 manufactured by Rigaku Corporation). In powder X-ray diffraction using $\text{CuK}\alpha$ -ray, the half value width of the diffraction peak on (110) plane at $2\theta=66.5\pm 1^\circ$ was 0.125° . The powder had an
5 apparent density of 3.26 g/cm^3 after pressed by an oil hydraulic pressing machine under 0.3 t/cm^2 . As a result of spectral analysis, titanium and fluorine were found to be localized on the surface. The positive electrode had a remaining alkali amount of 0.02 mass%.

10 The above LiCoO_2 mixed powder, acetylene black and a polyvinylidene fluoride powder were mixed in a mass ratio of 90/5/5, and N-methylpyrrolidone was added thereto to prepare a slurry, which was coated on one side of an aluminum foil having a thickness of $20 \mu\text{m}$ by using a
15 Doctor Blade. After drying, roll press rolling was carried out five times to prepare a positive electrode body sheet for a lithium battery.

Then, using one punched out from the positive electrode body sheet as a positive electrode, using a
20 metal lithium foil with a thickness of $500 \mu\text{m}$ as a negative electrode, using $20 \mu\text{m}$ of a nickel foil as a negative electrode current collector, using a porous polypropylene with a thickness of $25 \mu\text{m}$ as a separator, and using as an electrolyte solution a $1\text{M LiPF}_6/\text{EC}+\text{DEC}$
25 (1:1) solution (it means a mixed solution of EC and DEC in a mass ratio (1:1) comprising LiPF_6 as a solute, the same applies hereinafter), two pieces of simplifying

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sealed cell type lithium batteries made of stainless steel were assembled in an argon globe box.

One of these batteries employing the EC+DEC (1:1) solution as the electrolyte solution was charged up to
5 4.3 V at a load current of 75 mA per 1 g of the positive electrode active material at 25°C, and discharged down to 2.5 V at a load current of 75 mA per 1 g of the positive electrode active material, whereby the initial discharge capacity was obtained. Further, the volume capacity
10 density was obtained from the density of the electrode layer and the capacity per weight. With respect to this battery, the charge and discharge cycle test was further carried out 30 times. As a result, the initial volume capacity density of the positive electrode layer at 25°C
15 at a voltage of from 2.5 to 4.3 V was 161 mAh/g-LiCoO₂, and the capacity retention ratio after 30 times of charge and discharge cycle, was 99.5%. Further, with respect to the other battery employing the EC+DEC (1:1) solution as the electrolyte solution, the other battery was charged
20 for 10 hours at 4.3 V, and then broken down in the argon globe box. The positive electrode body sheet was picked up after charge, and after the positive electrode body sheet was washed, it was punched out at a radius of 3 mm, and then sealed in an aluminum capsule with EC. And
25 then, it was heated at a rate of 5°C/min by using a scanning differential calorimeter, whereby the heat generation starting temperature was measured. As a

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result, the heat generation starting temperature of the 4.3 V charged product was 178°C.

EXAMPLE 14

In the same manner as in Example 1 except that no
5 small particle size cobalt hydroxide was used and large
particle size tricobalt tetraoxide alone was used as a
cobalt source in Example 12, LiCoO_2 was synthesized. The
tricobalt tetraoxide and the cobalt carbonate were
blended in such a mixture ratio that the composition
10 would be LiCoO_2 after firing. The obtained LiCoO_2 powder
had an apparent density of 2.95 g/cm³ after pressing. As
a result, the initial weight capacity density at 25°C at
from 2.5 to 4.3 V was 161 mAh/g- LiCoO_2 , and the capacity
retention ratio after 30 times of charge and discharge
15 cycle was 97.2%. Further, the heat generation starting
temperature of a 4.3 V charged product was 162°C.

EXAMPLE 15

A positive electrode active material was synthesized
in the same manner as in Example 13 except that aluminum
20 hydroxide was used instead of titanium oxide in Example
13. As a result of chemical analysis, the positive
electrode active material was found to be
 $\text{LiCo}_{0.997}\text{Al}_{0.003}\text{O}_{1.998}\text{F}_{0.002}$, and the powder had a press
density of 3.25 g/cm³. Further, aluminum and fluorine
25 were found to be present on the surface. The remaining
alkali amount was 0.02 mass%.

The initial capacity was 160 mAh/g, the capacity

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retention ratio after 30 cycles was 99.3%, and the heat generation starting temperature was 179°C.

EXAMPLE 16

A positive electrode active material was synthesized
5 in the same manner as in Example 13 except that magnesium hydroxide was used instead of titanium oxide in Example 13. As a result of chemical analysis, the positive electrode active material was found to be
 $\text{LiCo}_{0.997}\text{Mg}_{0.003}\text{O}_{1.998}\text{F}_{0.002}$, and the powder had a press
10 density of 3.25 g/cm³. Further, magnesium and fluorine were found to be present on the surface. The remaining alkali amount was 0.02 mass%.

The initial capacity was 161 mAh/g, the capacity retention ratio after 30 cycles was 99.7%, and the heat
15 generation starting temperature was 187°C.

EXAMPLE 17

A positive electrode active material was synthesized in the same manner as in Example 13 except that zirconium oxide was used instead of titanium oxide in Example 13.
20 As a result of chemical analysis, the positive electrode active material was found to be $\text{LiCo}_{0.997}\text{Zr}_{0.003}\text{O}_{1.998}\text{F}_{0.002}$, and the powder had a press density of 3.26 g/cm³. Further, zirconium and fluorine were found to be present on the surface. The remaining alkali amount was 0.02
25 mass%. By using this powder, in the same manner as in Example 1, a positive electrode was produced, batteries were assembled, and the properties were measured. The

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initial capacity was 160 mAh/g, the capacity retention ratio after 30 cycles was 99.5%, and the heat generation starting temperature was 174°C.

[Effects of the Invention]

5 According to the present invention, a positive electrode active material for a lithium secondary battery, which has a large volume capacity density, has a high safety, is excellent in uniform coating properties, and is excellent in charge and discharge cyclic
10 durability and low temperature characteristics, a positive electrode for a lithium secondary battery employing it, and a lithium secondary battery, are provided.

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[TYPE OF DOCUMENT] ABSTRACT

[SUMMARY]

[OBJECT]

5 A positive electrode active material for a lithium secondary battery containing a lithium-cobalt composite oxide, which has a large volume capacity density, has a high safety and is excellent in charge and discharge cyclic durability, and its production process, are provided.

10 [MEANS OF ACCOMPLISHING THE OBJECT]

A positive electrode active material for a lithium secondary battery, which comprises a lithium-cobalt composite oxide represented by the formula $\text{Li}_p\text{Co}_x\text{M}_y\text{O}_z\text{F}_a$ (wherein M is a transition metal element other than Co or an alkaline earth metal element, $0.9 \leq p \leq 1.1$, $0.980 \leq x \leq 1.000$, $0 \leq y \leq 0.02$, $1.9 \leq z \leq 2.1$, $x+y=1$ and $0 \leq a \leq 0.02$) and comprising a mixture containing substantially spherical large particles of lithium-cobalt composite oxide having an average particle size D50 of from 7 to 20 μm and small particles of lithium-cobalt composite oxide having an average particle size D50 of from 10 to 30% of D50 of the large particles, wherein a mass ratio of the large particles/the small particles is from 1/2 to 9/1.

[SELECTED FIGURE]

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